

Persistence of molecular excitations in metallic fullerenes and their role in a possible metal to insulator transition at high temperatures

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We present ^{13}C NMR spin-lattice relaxation measurements ($1/T_1$) in $\text{Na}_2\text{CsC}_{60}$ and Rb_3C_{60} from 10 to 700 K. The large temperature range of this measurement allow to define unambiguously an increase of $1/T_1T$ with increasing temperature, which is anomalous in a simple metallic picture, where the Korringa law predicts $1/T_1T = \text{cst}$. We attribute this increase to the existence of an additional relaxation channel related to singlet-triplet (ST) excitations of Jahn-Teller distorted C_{60}^{2-} and C_{60}^{4-} . These units are formed within the metal on very short time scales (10^{-14} sec) that do not imply static charge segregation. We show that the amplitude of the ST component depends directly on the density of states, which indicates an interplay between metallic and molecular excitations. Such an interaction is also revealed by the high temperature behavior of $\text{Na}_2\text{CsC}_{60}$ and CsC_{60} , that we then discuss. A divergence between the behaviors of $1/T_1$, the NMR shift and the ESR susceptibility is interpreted as the result of a rapid increase of the lifetime of the charge carriers, signaling a tendency to charge localization. In our analysis, the particular stability of C_{60}^{2n-} is then a common feature of all known metallic fullerenes and allow to reconcile apparently contradicting properties of these systems.

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I. INTRODUCTION

The properties of strongly correlated materials have been in the focus of solid-state research for many years. To describe the competition between Coulomb and kinetic energies, the one band Hubbard model is widely used. However, many real systems exhibit orbital degeneracy, which adds a degree of freedom that is not always taken into account. Fullerenes are one such example as the lowest unoccupied molecular orbital that forms the narrow t_{1u} conduction band in the solid is triply degenerate. Together with the strong electron-phonon coupling characteristic of these materials, this leads to the possibility of Jahn-Teller distortions (JTD). Whereas predictions for the JTD can be done quite accurately for a single molecule¹, their role in the solid is less clear. The broadening of the molecular levels should at first sight reduce the gain of energy associated to JTD. As it is estimated to be of the same order of magnitude than the gap opened by the JTD, the survival of these distortions in the solid can be questioned.

Yet, JTD appear to play a crucial role in many different fullerenes. This paper concludes a serie of three papers devoted to NMR studies of different stoichiometries of alkali fullerenes, where we have already seen evidence for such effects. It is widely believed that JTD contribute to turn Na_2C_{60} and A_4C_{60} , which should be metals in a band picture, into non-magnetic insulators. In our first paper (called hereafter paper I²), we have presented NMR data supporting this scenario and we refer the reader to references therein to the various pa-

pers invoking JTD in the properties of A_4C_{60} . Perhaps more surprisingly, they offer the most likely way for explaining the unexpected properties of the cubic quenched (CQ) phase of CsC_{60} , the only alkali cubic metallic fullerene phase known so far besides A_3C_{60} . In this phase, we have shown in ref.³ and paper II⁴ that the electronic properties are inhomogeneous on the local scale because spin-singlets are trapped on about 10% of the C_{60} balls. We believe that these singlets are stabilized by a JTD of the C_{60} ball which is energetically more favorable for C_{60}^{2-} than C_{60}^{-} .

More generally, a simplified view of the effect of JTD on the t_{1u} band as a function of its filling is sketched on Fig. 1. The gain of energy obtained from the JTD is found to be always larger for evenly charged C_{60} . Then, JTD could induce attractive interactions for odd stoichiometries in order to promote the formation of the more stable C_{60}^{2n-} (hence, the presence of spin-singlet in CQ CsC_{60}), whereas for even stoichiometries, they would induce repulsive interactions and favor localization (hence, the insulating Na_2C_{60} and A_4C_{60}). This suggests an elegant way for rationalizing the different properties of even and odd stoichiometries^{1,5,6} and the purpose of this paper is to determine to what extent this framework could be relevant for A_3C_{60} , extending ideas already presented in for the case of $\text{Na}_2\text{CsC}_{60}$ ⁸.

Despite the possible survival of these unusual molecular properties in the solid, there is a general consensus that the electronic properties of A_3C_{60} can be understood in a rather conventional way, both for the metallic and superconducting states⁹. In the first part of this paper, we show that there are however in A_3C_{60} devi-

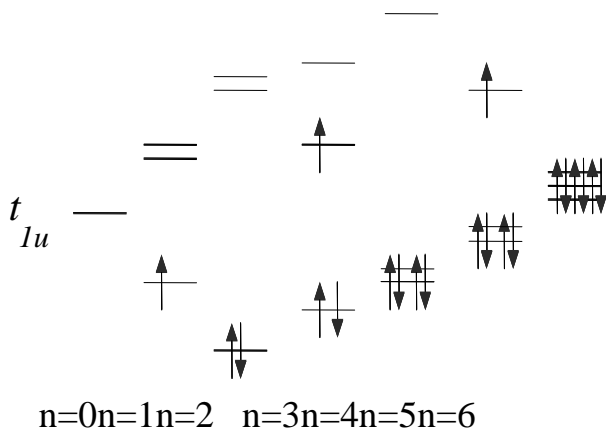


FIG. 1: Schematic representation of the splitting of the t_{1u} levels as a function of the C_{60} charge induced by Jahn-Teller distortions (adapted from ref.^{1,7}). Only the most stable JTD is represented.

ations with respect to the conventional metallic NMR behavior, that we attribute to an enhanced stability of C_{60}^{2-} and C_{60}^{4-} . The consequences of the formation of such “pairs” on the properties of the metal is an interesting issue to clarify. For this study, we choose two examples of superconducting fullerides Rb_3C_{60} ($T_c = 29$ K) and Na_2CsC_{60} ($T_c = 12$ K). While the structure of Rb_3C_{60} is face centered cubic (fcc , space group $Fm\bar{3}m$) through the whole temperature range¹⁰, Na_2CsC_{60} undergoes an orientational transition from fcc to simple cubic (sc , space group $Pa\bar{3}$) around 300 K¹¹. In the second part of this paper, we study the high temperature properties of two metallic fullerides where C_{60}^{2-} have been detected, Na_2CsC_{60} and CsC_{60} . The behavior departs from the one of a metal and can be best described by a progressive localization of the charge carriers with increasing temperature. This is likely related to a change of the role of the JTD as a function of temperature. However, the most important conclusion of this study might be that it reveals an overall similar behavior in these two compounds, which simplifies greatly the understanding of fullerides by unifying apparently conflicting properties. Up to now, CsC_{60} was thought to be metallic in its low temperature phase¹² and insulating in its high temperature phase¹³. The connection between these two behaviors was not understood, which has forbidden so far a comparison with A_3C_{60} systems.

II. DETECTION OF MOLECULAR EXCITATIONS THROUGH SPIN-LATTICE RELAXATION MEASUREMENTS IN SUPERCONDUCTING FULLERIDES

In this part, we demonstrate that the deviation of $1/T_1T$ from the simple metallic behavior can be convincingly attributed to singlet-triplet distortions of JTD C_{60}^{2-} and C_{60}^{4-} . To establish this, we discard in the first

part other possible origin for this deviation. In the second part, we give a quantitative analysis of the coexistence between metallic relaxation and singlet-triplet excitations, which sets this model on a firm basis.

A. Origin of the non-Korringa relaxation

In a metal, the relaxation of nuclear spins is usually dominated by their coupling with conduction electrons. This leads to a simple dependence of the relaxation rate on the density of states $n(E_f)$, known as the Korringa law¹⁴.

$$\frac{1}{T_1T} = \frac{\pi k_B}{\hbar} A^2 n(E_f)^2 \quad (1)$$

where A is the hyperfine coupling (in erg) between ^{13}C and conduction electrons. One anomaly in the NMR behavior of A_3C_{60} is that $1/T_1T$ frequently deviates from the $1/T_1T = \text{cst}$ law that one consequently expects. An increase of ^{13}C NMR $1/T_1T$ with increasing temperatures has been reported for nearly all A_3C_{60} compounds^{15,16,17,18}, sometimes with moderate values (30 % in Rb_3C_{60} ¹⁵) or very large ones (200% in Na_2CsC_{60} ¹⁷). To probe these aspects further, we have taken data in these two extreme cases in identical experimental conditions, with a 7 T applied magnetic field and standard saturation recovery pulse sequences, and over an extended temperature range. The results are presented on Fig. 2. In both compounds, the relaxation curves for the NMR magnetization are not exponential below 150 K, which causes *a priori* a problem for defining T_1 at low temperatures. However, we have shown in paper I that the non-exponentiality is small and does not change between 10 and 150 K so that it cannot affect significantly these results. Moreover, the region below 150 K is precisely the one where the Korringa law is better obeyed. For the data presented here, T_1 has been defined below 150 K as the mean value of a double exponential fit.

The narrow peak observed at 180 K in Na_2CsC_{60} is due to a coupling with slowing down molecular motions, as was also observed in the isostructural Na_2C_{60} ². As this shows that not only conduction electrons can contribute to the relaxation in our case, one could wonder whether similar peaks could be present (although not well resolved) in other temperature ranges or in Rb_3C_{60} . If so, could they explain part of the increase of $1/T_1T$? The large temperature range for the data presented here allow to discard such a possibility, because these peaks would be symmetric while the increase of $1/T_1T$ is essentially step-like. We refer the reader to our paper I for a detailed discussion of the characteristics of these molecular motion peaks.

From Eq. 1, some temperature dependence of $1/T_1T$ could be expected if $n(E_f)$ is not strictly constant as expected for a standard Pauli susceptibility. This could indeed happen, if there are narrow features in the density

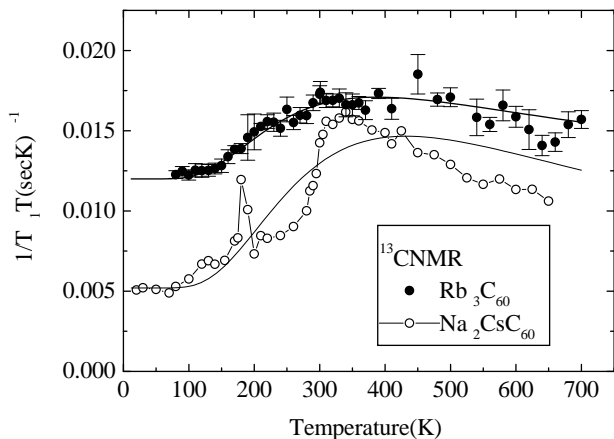


FIG. 2: ^{13}C NMR $1/T_1 T$ as a function of the temperature for Rb_3C_{60} and $\text{Na}_2\text{CsC}_{60}$. The thick line (Rb_3C_{60}) and thin line ($\text{Na}_2\text{CsC}_{60}$) are fits to the Eq. 2 of the text. The parameters are displayed in Table 1.

of states near the Fermi level. Those could be progressively disclosed as thermal expansion increases the lattice constant with increasing temperature. Because they are molecular solids, bound by weak Van der Waals interactions, fullerenes are actually very compressible materials and the temperature dependence of $n(E_f)$ must be seriously considered. Some studies have concluded that it is sufficient to explain the observed increase of $1/T_1 T$ for certain compounds¹⁸. An obvious test to determine if the increase of $1/T_1 T$ is due to such an effect is to plot $1/T_1 T$ together with χ^2 , as we have done for $\text{Na}_2\text{CsC}_{60}$ in ref.⁸. We have found that the temperature dependence of χ^2 is much too small to explain that of $1/T_1 T$, so that the deviation must be due, at least in this case, to the presence of an *additional relaxation channel*.

We want to reinforce this conclusion here by taking advantage of the comparison between $\text{Na}_2\text{CsC}_{60}$ and Rb_3C_{60} , over the large temperature range of the present experiments. The accuracy of the data presented on Fig. 2 at low temperature establishes that the increase is not regular. While $1/T_1 T$ is quite remarkably constant below 100 K ($\text{Na}_2\text{CsC}_{60}$) or 150 K (Rb_3C_{60}), it then increases up to room temperature, where it decreases ($\text{Na}_2\text{CsC}_{60}$) or saturates (Rb_3C_{60}). The lattice contraction on the other hand is expected to follow a smooth temperature dependence defined by the compressibility of the materials. Furthermore, the compressibility of *sc* and *fcc* phases are known to be quite similar¹⁹, so that the slightly different structure in the two compounds cannot explain such a difference. The thermal compressibility measured in Rb_3C_{60} ($\kappa = d(\ln a)/dT = 3.10^{-5} \text{ K}^{-120}$) corresponds to an increase of the lattice parameter a by 0.16 Å between 10 and 400 K, very close from the one measured in $\text{Na}_2\text{CsC}_{60}$ (0.14 Å¹¹). One could argue that even though the temperature dependence of a is the same, $n(E_f)$ might display quite different variations with a in *sc* or *fcc* materials²¹. This

idea has been proposed to explain the different variation of T_c with a in $\text{Na}_2\text{AC}_{60}$ (*sc*) or A_3C_{60} (*fcc*) materials (with $\text{A} = \text{K}, \text{Rb}, \text{Cs}$) because it is generally assumed that T_c depends on $n(E_f)$ in a straightforward way according to BCS theory. However, the variation of T_c with pressure was later found the same in *fcc* and *sc* phases²², so that the different variation of T_c is not related to $n(E_f)$ but to an alkali effect. The comparison between $\text{Na}_2\text{CsC}_{60}$ and Rb_3C_{60} is then legitimate and presents the advantage to cover a large variation in density of states. An even more serious drawback with such an explanation is that our study evidences a much larger increase in $\text{Na}_2\text{CsC}_{60}$ than in Rb_3C_{60} , although a direct measurement of the susceptibility below 300 K shows the opposite behavior²³.

B. Singlet-triplet excitations in A_3C_{60}

In $\text{Na}_2\text{CsC}_{60}$, the origin of the increase of $1/T_1 T$ was suggested by the comparison with Na_2C_{60} , which exhibits a very similar relaxation behavior at high T despite it is insulating (see⁸ or Fig. 7). In this latter compound, the relaxation is due to singlet-triplet transitions between different JTD of a C_{60}^{2-} . Theoretical calculations have shown that for an isolated C_{60}^{2-} , a JTD with a triplet ground state lies above the singlet JTD represented in Fig. 1 by $E_a=140$ meV, so that triplet states can be thermally populated¹. Therefore, we have suggested that *singlet-triplet excitations persist in $\text{Na}_2\text{CsC}_{60}$* because C_{60}^{2-} and C_{60}^{4-} are formed there on very short time scales (about 10^{-14} sec), which creates an additional relaxation channel explaining the increase of $1/T_1 T$ at high temperature. We now investigate if such an explanation could describe the evolution of the relaxation behavior between $\text{Na}_2\text{CsC}_{60}$ and Rb_3C_{60} .

The data led us to suggest that the relaxation can be divided between two relaxation channels, a metallic Korringa-like channel and a molecular channel corresponding to localized singlet-triplet excitations. For this latter term, we assume that the imaginary part of the susceptibility, the quantity measured by $1/T_1$ at the nuclear Larmor frequency (80 MHz for ^{13}C in this measurement), can be described by a Lorentzian with a width $1/\tau$, where τ is a lifetime characterizing the electronic excitations. This is a usual assumption for localized magnetic moments, which yields for small ω , $1/T_1 \propto \chi\tau$, where χ is the static paramagnetic susceptibility of the localized moment²⁴. This leads to the following expression.

$$\frac{1}{T_1 T} = \frac{k_B}{\hbar} A^2 \left(\pi n(E_f)^2 + \frac{\chi_{ST} \tau_{st}}{\mu_B^2 \hbar} \right) \quad (2)$$

where τ_{st} is the characteristic lifetime of a triplet state and χ_{ST} an activated susceptibility describing the population of triplet states. The separation between the two terms is quite arbitrary, as the same electrons participate to both terms. Such a phenomenological decomposition

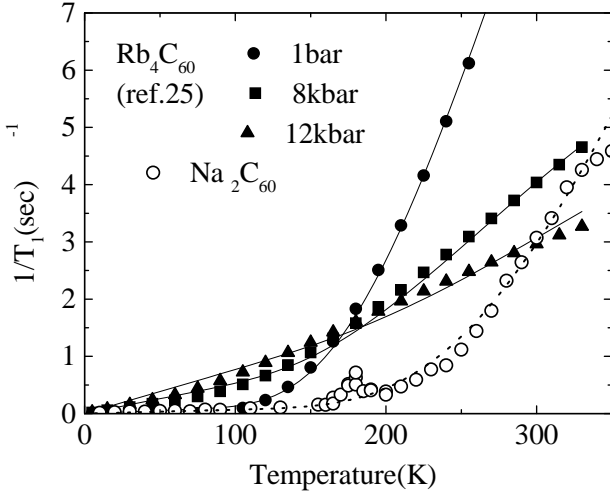


FIG. 3: ^{13}C NMR $1/T_1$ in Rb_4C_{60} for different applied pressure (from ref.²⁵) and Na_2C_{60} . The curves are fitted to Eq. 2 with parameters displayed in Table 1. They assume that the relaxation is the sum of a linear metallic component and an activated molecular one with fixed ratio.

should nevertheless capture the essential points of the physics as long as τ_{st} is shorter than the lifetime τ_p of a C_{60}^{2n-} in the metal. Some correlation between the parameters describing the “localized” states (like τ_{st}) and the extended carriers states (like $n(E_f)$) can be expected as a result of this situation.

A source of inspiration for this correlation is the evolution of Rb_4C_{60} from an insulator to a metal with applied pressure²⁵. This transition is not sharp, but a linear metallic term appears with increasing pressure *that coexists* with the localized activated one, as replotted on Fig. 3. As the metallic term grows, the molecular one can still be described by the same model, but the value of the gap and τ_{st} have to be reduced. This legitimates the assumption of coexisting molecular and metallic excitations, which is also observed in Na_2C_{60} ². We believe that this property is actually essential to understand the originality of fullerenes, in which molecular features are retained because the large electronic correlations forces one electron to spend a “long” time on each molecule before being transferred to the next.

The behavior in Rb_4C_{60} tells us that τ_{st} directly depends on $n(E_f)$. This suggests that *the triplet states are relaxed by conduction electrons*. Assuming that the triplet state can be treated as a local impurity on the timescale of its existence, we can use relaxation laws observed for localized impurities in a metal, that are analogous to a Korringa-like process²⁴.

$$\frac{1}{\tau_{st}} = \frac{\pi}{\hbar} k_B T J^2 n(E_f)^2 \quad (3)$$

where J would be the coupling between the triplet and conduction electrons.

To test this model, which reduces the number of free parameters in Eq. 2, we have tried to reproduce the pres-

sure evolution of the two terms in Rb_4C_{60} . To modelize the susceptibility associated with singlet-triplet excitations, we choose

$$\chi_{st} = \frac{8\mu_B^2}{k_B T} * \frac{\exp(-\Delta/T)}{2 + 3 \exp(-\Delta/T)} \quad (4)$$

which was found in reasonable agreement with the susceptibility of Na_2C_{60} ². The coupling J is treated as a shared parameter between the three sets of data and the best fits are found for $J = 10^{-13}$ erg. Fits using equations 2, 3 and 4 with this value for J are shown on Fig. 3. They are in fair agreement with the data, which supports this model. The density of states and the value of the gap used in each case are displayed in Table 1. This model can be applied as well to Na_2C_{60} . Fig. 3 shows that, with a larger gap value already noticed previously⁸ but keeping the same value for J , the data are also well reproduced.

Does this model also apply to the case of A_3C_{60} ? Eq. 3 implies that the increase of $1/T_1 T$ due to the localized term should show up more clearly when $n(E_f)$ is small, which is in qualitative agreement with the evolution of $1/T_1 T$ between $\text{Na}_2\text{CsC}_{60}$ and Rb_3C_{60} . Remarkably, the previous fitting procedure *with the same J value* gives a correct order of magnitude for the increase of $1/T_1 T$ in both compounds. In this model, the magnitude of the high temperature increase of $1/T_1 T$ is uniquely fixed by its value at low temperature. The best fits displayed on Fig. 2 with the parameters given in table 1 show an excellent agreement in the case of Rb_3C_{60} but is poorer for $\text{Na}_2\text{CsC}_{60}$. In this latter compound, it seems that a different regime is relevant for high temperatures, which will be discussed in the next section. Even below 300 K, the increase of $1/T_1 T$ cannot be ascribed to a single gap value. Similar problems were encountered in the case of Na_2C_{60} , which led us to suggest in paper I that the equilibrium between different JTD could be modified by changes in details of the structure as a function of temperature.

To check the consistency of our analysis, the triplet relaxation time τ_{st} should be compared to the lifetime τ_p of the C_{60}^{2n-} . This latter time can only be longer than the average time spent by one electron in the vicinity of a C_{60} ball τ_m . A lower bound for τ_m can be estimated by the time required for an electron to travel at the Fermi velocity from one ball to the other, $\tau_m = a / v_f \approx \hbar n(E_f)$. This is calculated in Table 1 and the comparison with τ_{st} deduced from the fits shows that they have similar order of magnitude at room temperature, so that this analysis is consistent. We note that we have used here the susceptibility given by Eq. 4, although one could assume that only a fraction of it, corresponding to the actual concentration of C_{60}^{2n-} in A_3C_{60} , should be used. This would give slightly longer value for τ_{st} .

Therefore, this simple model gives an overall satisfying description of the relaxation behavior in these compounds. The correlation between the molecular and metallic term might however be even more intricate. We

	Rb ₄ C ₆₀			Na ₂ C ₆₀	Na ₂ CsC ₆₀	Rb ₃ C ₆₀
	1 bar	8kbar	12kbar			
χ_m (10^{-4} emu/mol)	1	3.1	3.7	1.3	3.1	4.7
Δ (meV)	90	80	100	125	85	75
$\tau_m = \hbar n(E_f)$ (10^{-15} sec)		6	7.2		6	9
$\tau_{st}(300K)$ (10^{-15} sec)	35.3	3.7	2.6	21	3.7	1.6

TABLE I: Parameters used in the fits shown on Fig. 2 and Fig. 3 based on Equation 2, 3 and 4. χ_m is deduced from $n(E_f)$ and Eq. 1 assuming an hyperfine coupling $A=4.10^{-20}$ erg. The absolute values of τ_{st} should only be taken as an order of magnitude because it is somewhat model dependent but the qualitative variation between different compounds is meaningful, as well as the condition $\tau_{st} \leq \tau_m$ which legitimates the use of this model for the metals.

have assumed that the JTD C_{60}^{2-} can be considered as an isolated molecular entity, even if it is restricted to a limited timescale. The fact that the gap value is not fixed, but tends to decrease with increasing $n(E_f)$ in compounds with identical structures like Na_2C_{60} and Na_2CsC_{60} , shows explicitly that there is a further correlation between the two terms. Δ is not purely a molecular value and a more sophisticated description, introducing for example a screening of the C_{60}^{2n-} by conduction electrons, would be required to describe completely this behavior.

In addition, we have mainly tried to explain so far the increase of $1/T_1T$ which roughly takes place between 200 and 300 K. At higher temperatures, Eq. 3 predicts a decrease of the lifetime of the triplet states as $1/T$. This could change the balance between the two relaxation channels as a function of temperature. The simple estimate that we have used for τ_m is also likely to break down at high temperature because it requires that the mean free path for the electronic motion l is longer than a . On the contrary, it is known that very small values for the mean free path are deduced from resistivity measurements for fullerenes at high temperature, like 1-2 Å at 500 K in Rb_3C_{60} ,²⁶. Therefore, we could expect complications at high temperature, that might reveal, on the other hand, valuable information on the charge transport in these materials and we turn to this topic in the next section.

III. ARE “METALLIC FULLERIDES” METALLIC UP TO HIGH TEMPERATURES ?

Some anomalies in the high temperature behavior of fullerenes have been noticed for a long time. In Rb_3C_{60} , the photoemission spectra at high temperature does not display a clear Fermi edge²⁷. In Na_2CsC_{60} , optical conductivity measurements indicate a disappearance of the Drude-like peak above 300 K²⁸. All this motivates us to investigate the high temperature region in more details and we indeed report here two cases, Na_2CsC_{60} and CsC_{60} , where the high temperature behaviors are far from that of a simple metal and are even suggestive of a localization of the charge carriers. For all the data

reported here, we have checked that the behavior is fully reversible with temperature, ensuring that there is no deterioration of the sample quality and/or stoichiometrie.

A. Na_2CsC_{60}

1. progressive localization of the charge carriers inferred from $1/T_1$ behavior

Fig. 2 shows that $1/T_1T$ decreases regularly from 300 to 700 K in the *fcc* phase of Na_2CsC_{60} . This is anomalous as among the two terms identified in the relaxation so far, the metallic and the singlet-triplet components, the first one is expected to yield a constant value and the second one an increase of $1/T_1T$ or a slight decrease depending on the precise value of the gap (see the fit of Fig. 2). In Rb_3C_{60} , there might be a similar anomaly above 500 K, where $1/T_1T$ is somewhat lower than the fitted curve, but this cannot be concluded unambiguously within experimental accuracy and in the following we focus on Na_2CsC_{60} .

As the use of $1/T_1T$ might introduce an artificial bias by emphasizing the metallic component, we have replotted on Fig. 4, $1/T_1$ for ^{13}C NMR, together with the result from ^{133}Cs NMR, which displays essentially the same temperature dependence, except for the molecular motion peak. In our case, the interpretation of these data is not straightforward as we do not know how to separate the metallic term from the ST component. Within the metallic framework of the Korringa law, a decrease of $1/T_1T$ would be assigned to a reduction in the density of states signaling the onset of a broad metal to insulator transition. If it is a change in the singlet-triplet component, it could be due to modifications of the apparent value of the gap as was observed in Na_2C_{60} . To find a way out of this problem, a comparison with the ESR susceptibility shown in the inset of Fig. 4 is helpful. In the susceptibility, both the metallic and singlet-triplet terms are also present but with different ratios as they are not weighted by the lifetime of the excitations, like $1/T_1$ is. χ is dominated at low T by a constant Pauli component and then increases up to 350 K, in our opinion mainly as a result of singlet-triplet excitations. Like $1/T_1T$, it

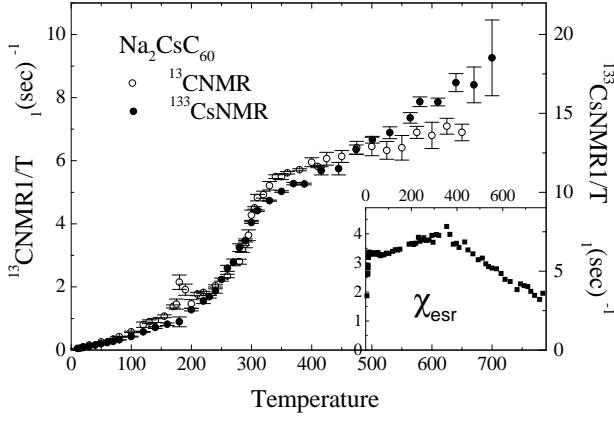


FIG. 4: $1/T_1$ for ^{13}C and ^{133}Cs in $\text{Na}_2\text{CsC}_{60}$ as a function of temperature. For ^{133}Cs , the recovery curves are exponential through the whole temperature range. Inset : ESR susceptibility as a function of temperature measured on a sample from the same batch.

is clearly anomalous above room temperature, where it starts decreasing sharply. This is very different from the behavior of χ in Na_2C_{60} , where it keeps increasing at high temperature, which tells us that a modification of the ST component alone cannot account for this result. Above 350 K, we observe a strong divergence in behavior between χ and $1/T_1$, χ falls far below the metallic value, whereas $1/T_1 T$ is still far above. This can only be understood if *the lifetime of the excitations diverges above room temperature*. This reminds of a situation observed at the transition between solid and liquid in X_2Te_3 ($\text{X}=\text{In}, \text{Ga}, \text{Sb}$)²⁹. Upon melting, the increasing disorder induces a progressive localization of the charge carriers that leads to a decrease of the Pauli susceptibility, due to the reduction of the carrier density. At the same time, $1/T_1 T$ is found to increase, as the lifetimes of the excitations increases rapidly. To account for this effect $n(E_f)^2$ in Eq. 2 has been replaced by the authors of ref²⁹, by $n(E_f)\tau_m/\hbar$, where τ_m is now free to deviate from the metallic value $\hbar n(E_f)$. In our case, both τ_m and/or τ_{st} could be responsible for the increase of $1/T_1 T$. However, in both cases, we can conclude that there is a *progressive localization of charge carriers*.

2. nature of the localized charge carriers inferred from the static NMR alkali spectra

If the localization process went as far as to correspond to a static charge separation, we could expect to observe changes in the NMR spectra as a result of inequivalent alkali sites neighboring a different number of C_{60}^{2n-} . This is the case in CQ CsC_{60} where a splitting of the Cs spectrum is observed at low temperature, corresponding to the localization of 10% C_{60}^{2-} , as discussed in details in paper II. In $\text{Na}_2\text{CsC}_{60}$, static charge separation can be ruled out because ^{133}Cs and ^{23}Na spectra consists of one fea-

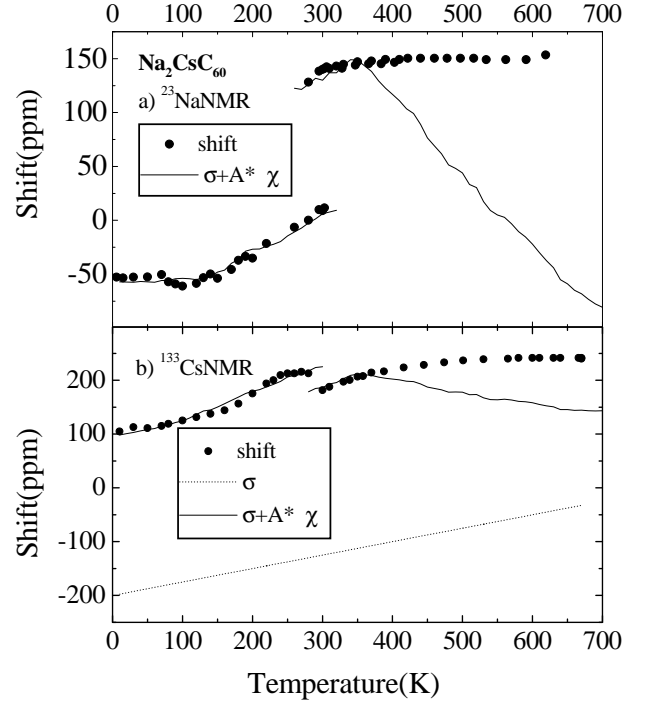


FIG. 5: Shift for ^{23}Na (part a) and ^{133}Cs (part b) in $\text{Na}_2\text{CsC}_{60}$. The discontinuity at 300 K is due to the structural transition from the orientationally ordered *sc* phase ($T < 300$ K) to the *fcc* one. ^{23}Na (resp. ^{133}Cs) shifts are measured with respect to a diluted NaCl (resp. CsCl) solution. The lines are comparison with the behavior of the susceptibility assuming values of hyperfine shift and chemical reference discussed in the text.

tureless narrow line (with the exception of the Na “T” line). This is consistent with the value given previously for τ_{st} which is much shorter than the NMR time scale (a few ms corresponding to the inverse width of the spectrum), so that a motional narrowing of the spectra should still take place even if τ_{st} increases by many order of magnitudes.

There are however clear anomalies in the alkali NMR which are revealed when comparing the shifts K for ^{133}Cs and ^{23}Na lines, presented on Fig. 5, together with the ESR susceptibility. A simple scaling between K and χ is expected, $K = \sigma + A\chi$, where A is the hyperfine coupling and σ a reference chemical shift. On Fig. 5, it can be seen that both nuclei sense an increase of the susceptibility between 150 K and 300 K, but they do not reproduce similarly the decrease seen by ESR above 300 K. This also suggests, although in a puzzling way, that the properties of the material are changing above room temperature. Let us now discuss quantitatively the behavior of the shift for the two nuclei.

a. ^{23}Na NMR In the *sc* phase, we can scale the ^{23}Na shift and the susceptibility, as shown by the line of Fig. 5a by using $\sigma = -300$ ppm and $A = 4500$ Oe/ μ_B . It is interesting to compare these numbers with those found for ^{23}Na NMR in paper I for the isostructural Na_2C_{60} , $\sigma = -$

65 ppm and $A = 2300 \text{ Oe}/\mu_B$. The difference for σ is quite large and not expected as σ essentially depends on the diamagnetism of the Na^+ filled orbitals which should not change much. To avoid this problem, it might be more realistic to assume that the hyperfine coupling to the metallic component is *smaller* than the one to localized excitations, maybe because Na moves a little bit towards the C_{60}^{2-} or C_{60}^{4-} , which increases the hyperfine coupling for this term. This automatically gives a value of σ closer to that of Na_2C_{60} , as the shift is dominated at low T by the metallic term.

Through the *sc-fcc* transition at 310 K, we have observed in Na_2C_{60} an increase by 30% of the hyperfine coupling probably associated to the change of structural environment of Na (see paper I). This is also clearly present in $\text{Na}_2\text{CsC}_{60}$. As a guide to the eye, we have plotted the variation of K that would be expected for ^{23}Na NMR from the one of χ assuming no change for σ and a continuous value for χ . This only emphasizes what was immediately clear, K does not follow the static susceptibility at high temperature, it is nearly constant while χ drops by a factor 2. Relying on the previous findings i) the characteristic lifetime of the localized excitations starts to increase above 300 K and ii) the hyperfine coupling to the localized excitations is particularly strong, we would like to conclude that the reason for the different behavior of K and χ at high temperature is due to *an increase of the hyperfine coupling associated with the progressive localization of the carriers*. Indeed, we know from CQ-CsC_{60} , studied in paper II, that the coupling can be very strong with localized singlets in a metallic environment. This enhancement disappears if all the balls are equivalent and bear a singlet, like in Na_2C_{60} , because Na has no reason to move towards a particular ball.

b. ^{133}Cs NMR The ^{133}Cs shift presents a similar behavior but it displays a significant temperature variation below 100 K, which does not appear in the ESR data. Such a linear temperature dependence of the shift has already been observed in the NMR of various alkali in fullerenes^{30,31,32}. Its origin is not well understood, but as it is not related to the electronic susceptibility³⁰, it is probably of orbital origin and we will include this linear variation in the chemical shift σ . Choosing $\sigma = -200 + 0.25 T$, as indicated on Fig. 5 by the dotted line, allows to extract an additional increase, clearly present between 150K and 300K which scales with the susceptibility with $A = 5000 \text{ Oe}/\mu_B$. As done for ^{23}Na , we then extrapolate the variation of K at high temperatures assuming that σ and χ do not change, which requires here a reduction of A in the *fcc* phase to $4500 \text{ Oe}/\mu_B$ ³³. Here-again, there is a significative difference between K and χ , although less dramatic than for Na. We also observe that the scaling between K and χ is not lost at the structural transition but at somewhat higher temperatures $T \approx 400 \text{ K}$, making it unlikely that the structural transition could be responsible for the change of the electronic properties of $\text{Na}_2\text{CsC}_{60}$. If the divergence between K and χ is to be attributed again to an increase of the hyperfine coupling,

this yields $A = 6000 \text{ Oe}/\mu_B$ at 650K, which corresponds to a 25 % increase from 350 K to 650 K. Such an increase should also enhance $1/T_1$, proportional to A^2 , by a factor 1.5. On Fig. 4, we see that ^{133}Cs $1/T_1$ indeed increases a little bit more rapidly than ^{13}C $1/T_1$ at high temperatures. As ^{13}C cannot move, its hyperfine coupling can be used as a reference for the “unenanced” value of $1/T_1$. This predicts $1/T_1 = 13 \text{ sec}^{-1}$ instead of the observed $1/T_1 = 17 \text{ sec}^{-1}$, which is close from a factor 1.5 and supports the idea of an enhancement of the hyperfine coupling³⁴.

In summary, many anomalies appear above 400 K in $\text{Na}_2\text{CsC}_{60}$, which gives evidence for a change in the electronic properties. Although, the data are conflicting at first sight, because different probes measure apparently different behaviors, we propose that this can be understood assuming that we enter an intermediate regime between metallic and localized behavior. In this regime, $1/T_1$ is dominated by the increase of the lifetime of the charge carriers around a particular C_{60} ball, which also modulates the value of the alkali hyperfine couplings. We cannot decide unambiguously whether the charge carriers are localized as C_{60}^{3-} or C_{60}^{2n-} . Both are consistent with the $1/T_1$ measurements. The change in the alkali hyperfine coupling somewhat favors C_{60}^{2n-} , as we could expect a larger motion of the alkali towards the differently charged C_{60} . The idea that a motion of the alkali ions, especially of the light Na ion, is playing an important role in the high temperature properties of this phase was already suggested in²⁸. However, we cannot rule out that the appearance of a localized charge is sufficient to trigger such a motion and modify the alkali hyperfine coupling regardless of the charge value.

Because we have detected in the previous part of this paper an important role of JTD in the metallic phase, it seems reasonable to associate the progressive localization at high temperatures with a conflict between the stabilization of JTD and the delocalization of the charge carriers. We can for example speculate that the population of many different distortions at high temperatures introduces disorder for the electronic system, which hinders the electronic motion. These electrons could then be localized as C_{60}^{3-} or C_{60}^{2n-} depending on the precise balance between Coulomb repulsion and Jahn-Teller attraction, but, more importantly, this behavior reveals by defect that a cooperation is required between JTD and electronic motion to obtain the metallic state. This agrees with the idea that JTD, at last at low temperatures, help the systems with odd stoichiometries to become metallic by stabilizing the C_{60}^{2n-} , which have to be formed as a byproduct of electronic jumps.

B. The high temperature cubic phase of CsC_{60}

Another very anomalous high-temperature phase is the one of CsC_{60} . It appears to have a Curie-like susceptibility³⁵, the ^{133}Cs NMR shift also follows a Curie

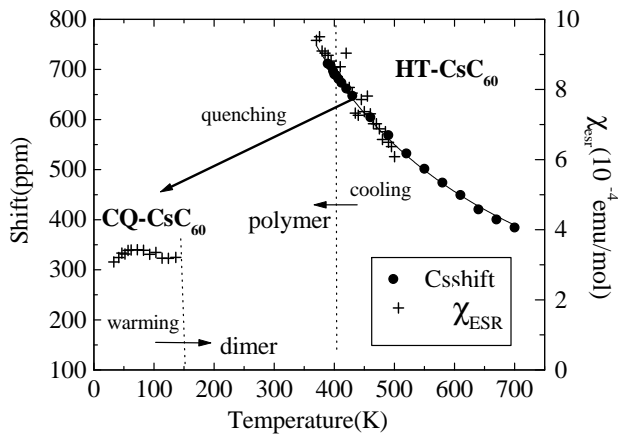


FIG. 6: ^{133}Cs NMR shift in the high temperature cubic phase of CsC_{60} (black points), the line is a fit to a Curie law. There are two cubic phases in CsC_{60} , a cubic quenched (CQ) metastable phase is stable only for $T < 130$ K, and a high temperature one ($T > 380$ K). In these two phases, crosses show the behavior of the ESR susceptibility to illustrate the change in electronic properties.

law within experimental accuracy and $1/T_1$ is nearly constant as expected for a paramagnetic insulator¹³. All of this was taken as evidence for electronic localization. As for NMR, we have checked that this behavior holds up to 700 K for the ^{133}Cs shift (see Fig. 6) and ^{13}C $1/T_1$ (see Fig. 7, actually T_1^{-1} is not really constant but decreases by 25 % from 400 K to 700 K).

Below 350 K, a structural transition takes place to a polymerized phase with very different properties. However, the cubic phase can be studied at low temperatures (below 130 K) by quenching the high temperature phase and it seems to be metallic. A Pauli susceptibility¹² and a Korringa law for ^{13}C NMR above 50 K³ are observed. The behavior of the susceptibility in the two phases are reported on Fig. 6 to illustrate this point. The difference is very puzzling, as the structure is the same except for the orientational order (the CQ phase of CsC_{60} is sc^{36} , while the high temperature phase is fcc). If this structural transition were to play a role in the conductivity, the high temperature phase, which is structurally equivalent to metallic A_3C_{60} , should be the more directly comparable to other fullerides, whereas it is this phase that displays “anomalous” properties. This distinct behavior in the two phases casts doubt on whether 1 electron in the t_{1u} band yields a metallic or insulating behavior.

On the other hand, it appears now quite similar to that of $\text{Na}_2\text{CsC}_{60}$ and it seems less difficult to connect the properties of the two CsC_{60} phases. $\text{Na}_2\text{CsC}_{60}$ also resembles a good metal at low temperature and, for some properties, particularly the ESR “Curie-like” susceptibility, an insulator above 300 K. If the data between 100 and 300 K were missing for $\text{Na}_2\text{CsC}_{60}$, one would also conclude that we are dealing with two entirely different phases. We have seen through this paper that including singlet-triplet excitations of JTD balls offers a convinc-

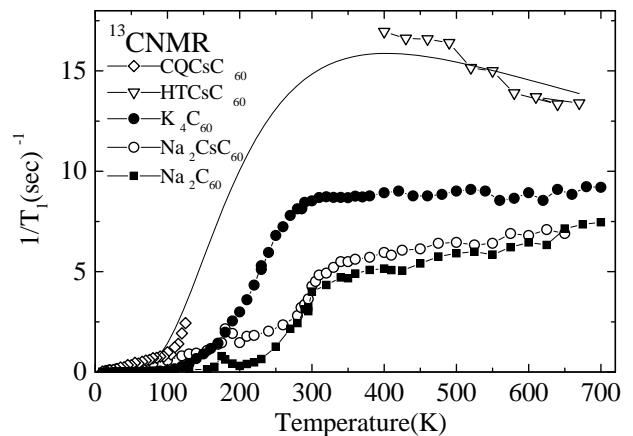


FIG. 7: Comparison of ^{13}C NMR $1/T_1$ in different fullerides showing a similar increase up to 300 K that we attribute to singlet-triplet excitations. The line connecting the cubic quenched (CQ) phase of CsC_{60} and the high temperature (HT) one is a fit to Eq. 2 given in the text.

ing way to explain this apparent discrepancy, and the same could be true for CsC_{60} . The underlying similarity is perhaps best illustrated by looking at the temperature dependence of $1/T_1$ for ^{13}C in various phases, as we do on Fig. 7. In this context, it is tempting to interpret the gap between the values of $1/T_1$ in the CQ phase and those of the high temperature phase by an increase due to a singlet-triplet component. In CQ CsC_{60} , just before the transition to the dimer phase, we do observe an increase of $1/T_1$, which might correspond to such a component. Adjusting a fit to Eq. 2 to these points and the high temperature value gives the line sketched on Fig. 7. This yields a smaller gap $\Delta = 50$ meV than for the other compounds, but this is consistent with the fact that $1/T_1$ decreases at high temperatures. Indeed, Fig. 7 shows a systematic relation between the value of the gap and the behavior at high temperature: the lower the gap, the higher $1/T_1$ and the smaller (eventually negative) the slope of its variation at high temperature. Qualitatively, this is not surprising as, with a small gap, the susceptibility is dominated at high temperature by the Curie law for the triplet states (see Eq. 4).

Putting these data together then gives a fairly good understanding of the CsC_{60} system. We know from our study of CQ CsC_{60} that JTD C_{60}^{2-} are formed at low temperatures but, presumably because there is no symmetric JTD for neutral C_{60} , they get localized on a small fraction of the C_{60} balls, contrary to C_{60}^{2-} in superconductors. The singlets start to move as the temperature increases and the lifetime of a C_{60}^{2-} in the metal decreases exponentially as shown in paper II. We can speculate that, if it were stable, the properties of cubic CsC_{60} would be very similar to those of a metal like $\text{Na}_2\text{CsC}_{60}$ between 100 K and 300 K and would evolve gradually towards an almost insulating state at high temperatures, which is the one observed above 400 K.

IV. CONCLUSION

To conclude, we have proposed in this paper that the metallic character of fullerides with an odd number of electrons per C_{60} is driven by the formation of pairs of electrons on very short time scales stabilized by Jahn-Teller distortions. We argue that the deviation of the NMR $1/T_1T$ from the canonical “metallic” Korringa law observed in many A_3C_{60} systems can be convincingly attributed to the presence of singlet-triplet excitations of these electronic pairs. By studying two superconducting metals with very different density of states, we evidence a dependence of the characteristic time τ_{st} of the triplet state for these pairs on $n(E_f)$ that makes the detection of singlet-triplet excitations easier in compounds with small density of states. This explains why the effect has not been clearly identified up to now, the molecular excitations being masked in the most heavily studied compounds like K_3C_{60} and Rb_3C_{60} .

We have then presented new data at high temperatures that show a clear evolution of the behavior of the electronic properties in at least two compounds Na_2CsC_{60} and CsC_{60} . In the first case, we interpret the breakdown of the scaling between various quantities at about 400 K as the onset of a progressive localization of the charge carriers. We suggest that this localization is due to a change of the status of JTD in the metal as the temperature increases. The localized charge carriers could either be the electronic pairs formed via JTD or independent electrons, depending on the precise nature of the high temperature evolution. A similar, probably slightly more efficient, localization takes place in CsC_{60} . Although this phase was already believed to be insulating, seeing this as a metal to insulator transition allow to connect its properties to those of the low temperature metallic phase. This adds greatly to the understanding of these systems, as all metallic phases can now be described within the same framework. JTD appear as a key ingredient in this

behavior, which makes it likely that the difference between even and odd stoichiometries, respectively insulating and metallic, is due to the sensitivity of Jahn-Teller distortions to the parity of the C_{60} charge. As recalled in Fig. 1, JTD are always a little bit more stable for even parity.

This work also raises new questions on the nature of charge transport in A_3C_{60} . If the enhanced lifetime of C_{60}^{2-} and C_{60}^{4-} is a general feature of A_3C_{60} , it is of course important to examine their role within the metal. The role that we assigned here to Jahn-Teller distortion is an example of how electronic properties are coupled to phonons and could be a first step towards the concept of polarons. However, we do not know how fast the JTD can adjust itself to a change of the charge of the molecule, produced by jumps of electrons from one ball to the other. The idea of a polaron would imply that one electron moves with a given JTD. In our case, we could as well assume that a JTD is fixed for a given molecule, regardless of its charge, which only increases the lifetime of favorable JTD C_{60}^{n-} configurations (namely n even). The lack of experimental knowledge about the time scale for the Jahn-Teller distortion, relatively to the motion of electrons, makes it difficult to discriminate between these possibilities. Nevertheless, some correlation between them is required to establish a coherent band-like charge transport. This could be destroyed with increasing temperature resulting in hopping like process. This might be what we witness in Na_2CsC_{60} and this bears interesting similarities to the metal to insulator transition observed at high temperature in manganites with ferromagnetic metallic ground states. In these systems also strong electronic correlations are coexisting with the possibility of JTD of the doubly degenerate e_g orbitals. It has been proposed that the occurrence of JTD at high temperatures, which forbids hopping in this case, adds to the double exchange mechanism to trigger a transition to the high temperature insulating phase³⁷.

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